

Multi-responsive nanocomposite hydrogels with high strength and toughness[†]

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Multi-responsive hydrogels with high strength have great significance for potential applications in smart soft devices. However, it remains a challenge to incorporate multiple responsive moieties with energy dissipation mechanisms. Herein, multi-responsive nanocomposite hydrogels with high compressive strength and toughness were synthesized via *in situ* copolymerization of *N*-isopropylacrylamide (NIPAM) and acryloyloxyethyltrimethyl ammonium chloride (DAC) in an aqueous dispersion of exfoliated LAPONITE® RDS with a minute amount of *N,N'*-methylenebisacrylamide (MBAA) as a crosslinker. The combined use of clay and MBAA is demonstrated to be favorable for the high strength and toughness, and helped in avoiding precipitation of clay nanosheets, which otherwise occurred upon addition of cationic DAC. The effect of the NIPAM/DAC molar ratio, MBAA and clay contents on the properties of the hydrogels has been systematically investigated. Compression tests showed a compressive strength up to 6.2 MPa, with fracture strain higher than 90%. The presence of ionic DAC moieties in the hydrogels rendered a very high swelling ratio up to 40 (g g⁻¹). These hydrogels were responsive to temperature changes due to the presence of NIPAM units, with the transition temperature (T_{trans}) dependent on the molar ratio of NIPAM and DAC monomers. The internal electrostatic repulsion of the NIPAM/DAC copolymer network changed upon exposure to solutions with different pH and/or ion strength. Cyclic swelling–shrinking was demonstrated by shuttling the gels between pure water and 0.1 mol L⁻¹ NaCl solution.

Introduction

Stimuli-responsive polymer hydrogels have been widely studied for decades¹ as promising functional soft materials^{2,3} for potential applications in sensors, actuators,⁴ drug delivery,⁵ separation,⁶ and biotechnological and tissue engineering devices.^{7,8} Among these, hydrogels responsive to changes in pH, ion strength, temperature, etc., have been widely investigated. For practical applications, adequate mechanical properties are needed, which have been challenging for weak and fragile conventional hydrogels. Besides, there is an increasing demand to combine two or more responsive mechanisms to achieve multi-responsive and multi-functional hydrogels.

Many strategies⁹ have been developed to create tough hydrogels including nanocomposite hydrogels,¹⁰ double network hydrogels,¹¹ slide ring hydrogels,¹² micelle-crosslinked hydrogels,¹³ hybrid hydrogels,¹⁴ etc. Among these, nanocomposite (NC) hydrogels, by using exfoliated clay nanosheets as physical crosslinkers to polymer chains, have shown extraordinary strength and toughness.¹⁰ Therein, the polymer chains are attached to exfoliated clay platelets, presumably through noncovalent interactions including hydrogen bonding.^{15–17} Reversible polymer chain detachment from and re-adsorption to clay surfaces are suggested to account for the excellent properties of NC gels including extraordinary tensibility, high transparency, and swelling/de-swelling properties.^{18–21} Such a nanocompositing concept has been advanced by using *N*-isopropylacrylamide (NIPAM) as a monomer to synthesize thermo-responsive hydrogels¹⁹ due to the well known lower critical solution temperature (LCST).²² More interestingly, it has recently been demonstrated that a subtle difference in clay content renders significant variations in swelling–deswelling upon changes in temperature, which is utilized to fabricate bilayer actuators as manipulators with well-defined structures.²³

Despite the outstanding mechanical properties, it has been difficult to introduce other responsive monomers, e.g., ionic monomers, into NC gels²⁴ because the high ionic strength

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unfavors the dispersion stability of exfoliated clay platelets carrying negative charges on the surface and positive charges on the rim.²⁵ Aggregation and gelation occur when the ionic monomer concentration or ionic strength of the LAPONITE® suspension becomes too high. Many studies have been attempted to resolve these problems. Negatively charged monomers including acrylic acid and sodium methacrylate (SMA)²⁶ have been used to prepare responsive NC hydrogels after modification of clay with non-ionic monomers, acid,²⁷ or 2-acrylamido-2-methylpropane-sulfonic acid (AMPS).^{28,29} In contrast, less is known about nanocomposite hydrogels with positive charges because positively charged monomers may cause precipitation due to the damage to electrostatic balance of the clay suspension. Instead, chargeable neutral monomers were used to gain positive charges in a polymer network by protonation after polymerization.^{16,30} In these cases, however, the pH responsive behavior is limited, particularly as both temperature sensitive and chargeable monomers are copolymerized to create dual responsive hydrogels.

In this study, we prepared multi-responsive nanocomposite hydrogels by copolymerizing NIPAM and cationic monomer acryloyloxyethyltrimethyl ammonium chloride (DAC) with the presence of exfoliated clay nanosheets. It aims to combine the thermo-responsiveness of NIPAM and the pH and ion responsiveness of a cationic DAC monomer.^{31,32} In order to avoid clay aggregation, a very small amount of *N,N'*-methylenebisacrylamide (MBAA) was added and adsorbed on the clay surface. As a result, the polymer chains were crosslinked through both noncovalent interactions with clay nanosheets and sparse chemical crosslinkers. The effects of MBAA content, clay content, and the NIPAM/DAC molar ratio on the mechanical properties, swelling, thermo-responsiveness, and ion-responsiveness of the hydrogels have been systematically investigated.

Experimental section

Materials

N-Isopropylacrylamide (NIPAM), acryloyloxyethyltrimethyl ammonium chloride (DAC), potassium persulfate (KPS), *N,N,N',N'*-tetramethylethylenediamine (TEMED), and *N,N'*-methylenebisacrylamide (MBAA) were purchased from Aladdin Chemical Incorporation (Shanghai, China) and used as received. Synthetic hectorite clay (LAPONITE® RDS) was kindly provided by Zhejiang Fenghong New Materials Inc.

Synthesis of nanocomposite hydrogels

The hydrogels were synthesized through *in situ* free radical copolymerization of NIPAM and DAC in an aqueous suspension of LAPONITE® RDS with minute MBAA as a chemical cross-linker. First, LAPONITE® was dispersed in Milli-Q water (100 mL) under stirring for 10 min. Then, NIPAM and MBAA were added to the clay suspension under stirring at room temperature, followed by ultrasonication for 1 h. Subsequently, aqueous solutions of initiator KPS (20 mg mL⁻¹) and DAC were separately added to the mixture solution under stirring in an ice water bath for 30 min. Finally, the catalyst, TEMED, was added to the reaction mixture

under stirring for 30 min before being injected into a mold with a 4 mm silicone spacer between two glass slides for free radical polymerization at 25 °C for 24 h.

In all experiments, the total monomer concentration was fixed at 1 mol L⁻¹. The molar ratio of monomers, initiator (KPS) and catalyst was 100 : 0.426 : 0.735. For comparison, hydrogels without MBAA or LAPONITE® were synthesized as controls.

The nanocomposite hydrogels are denoted as N_mD_nL_xM_y, with N for NIPAM, D for DAC, L for LAPONITE®, and M for MBAA. Subscript *m* represents the mol% of NIPAM, *n* for DAC, *x* for the mass fraction of LAPONITE® and *y* is the mol% of MBAA.

Mechanical tests

Tensile tests were conducted on 2 mm × 4 mm × 50 mm samples of as-prepared gels by using an Instron 5567 mechanical testing machine equipped with a 500 N load cell (Instron Inc, USA) at room temperature. The gauge length was 25 mm, and the crosshead speed was 25 mm min⁻¹. The tensile strain was calculated as the length change relative to the initial length of the specimen, and the engineering tensile stress was evaluated based on the area of the initial cross section. Five specimens were tested for each material and the results were reported as mean ± standard deviation (SD).

Compression tests were conducted on as-prepared cylindrical hydrogel samples (approximately 8 mm in diameter and 8 mm long, *n* = 5 each) in an unconfined mode at 2.0 mm min⁻¹ by using the Instron 5567 mechanical testing machine equipped with a 10 kN load cell. The compression strain limit was set as 98% to protect the load cell. The results were reported as mean ± SD.

Swelling and stimuli-responsiveness

The as-prepared hydrogels (initial size of 5.0 mm diameter × 5.0 mm thickness) with an initial weight *W*₀ were immersed in pure water, with the weight at time *t* (*W*_{*t*}) determined by a balance at room temperature. The swelling ratio was defined as *W*_{*t*}/*W*₀.

In order to examine the responsive behavior to changes in pH or ion strength, the as-prepared hydrogels were immersed in pure water at different temperatures, or with different pH or ion concentrations at room temperature. The swelling ratio was recorded over time.

In order to study the temperature-responsiveness, the as-prepared hydrogels were immersed in water at different temperatures for swelling/deswelling until equilibrium. The swelling ratio at each temperature was normalized by that at 20 °C, and plotted as SR_{*T*}/SR₂₀ vs. temperature.

Results and discussion

Synthesis of p(NIPAM-*co*-DAC)/LAPONITE® nanocomposite hydrogels

In order to synthesize tough hydrogels responsive to temperature, pH, and ion strength, two functional monomers, NIPAM and DAC, were copolymerized with the presence of exfoliated LAPONITE® nanosheets as physical crosslinkers and toughening agents. Besides, it is critical to use MBAA as a chemical crosslinker in addition to clay. Herein, LAPONITE® nanosheets were fully

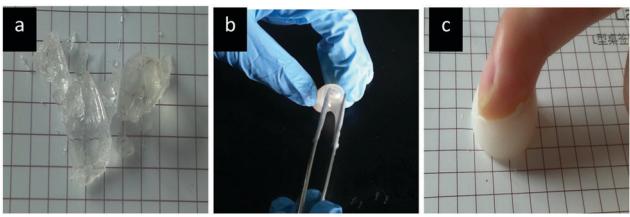


Fig. 1 Photographs of (a) MBAA-crosslinked pNIPAM gel after loading, (b) p(NIPAM-co-DAC) gel without clay, and (c) N_{0.75}D_{0.25}L₅M_{0.5} hydrogel.

exfoliated, according to X-ray diffraction patterns of the obtained hydrogels (Fig. S1, ESI†). Meanwhile, the cationic DAC monomer concentration was lower than 0.05 mol L⁻¹, and no clay aggregation was observed prior to or during polymerization. In two control experiments, MBAA-crosslinked p(NIPAM-co-DAC) gels were very fragile and could not sustain the swelling (Fig. 1a). Without MBAA, on the other hand, the p(NIPAM-co-DAC)/clay mixture became highly viscous but no hydrogels were obtained (Fig. 1b). With the addition of a very small amount of MBAA as an additional chemical crosslinker, tough hydrogels were obtained. A series of hydrogels (Table 1) were synthesized in order to investigate the effects of MBAA content, clay content, and the NIPAM/DAC ratio on the swelling, mechanical properties, and responsiveness of the gels. In contrast to the transparent nanocomposite hydrogels synthesized by Haraguchi *et al.*,²⁰ these hydrogels appear opaque, despite the well exfoliation and dispersion of clay, probably due to the phase separation between the less hydrophilic PNIPAM segments and the highly hydrophilic PDAC segments, which may be frozen during gelation and form microdomains.^{33,34}

Swelling behavior of the nanocomposite hydrogels

The swelling of hydrogels has been systematically investigated as a function of MBAA content, clay content, and the NIPAM/DAC ratio.

Table 1 Synthesis formulations of the poly(NIPAM-co-DAC)/clay nanocomposite hydrogels

Hydrogels	NIPAM (mol L ⁻¹)	DAC (mol L ⁻¹)	Clay (g per 100 mL)	MBA (mmol per 100 mL)
N _{0.75} D _{0.25} M ₁₀	0.75	0.25	0	10
N _{0.75} D _{0.25} L ₅ M ₁₀	0.75	0.25	5	10
N _{0.75} D _{0.25} L ₅ M ₅	0.75	0.25	5	5
N _{0.75} D _{0.25} L ₅ M ₄	0.75	0.25	5	4
N _{0.75} D _{0.25} L ₅ M ₂	0.75	0.25	5	2
N _{0.75} D _{0.25} L ₅ M ₁	0.75	0.25	5	1
N _{0.75} D _{0.25} L ₅ M _{0.5}	0.75	0.25	5	0.5
N _{0.75} D _{0.25} L ₅ M _{0.1}	0.75	0.25	5	0.1
N _{0.75} D _{0.25} L ₂ M ₅	0.75	0.25	2	0.5
N _{0.75} D _{0.25} L ₃ M _{0.5}	0.75	0.25	3	0.5
N _{0.75} D _{0.25} L ₄ M _{0.5}	0.75	0.25	4	0.5
N _{0.75} D _{0.25} L ₅ M _{0.5}	0.75	0.25	5	0.5
N _{0.75} D _{0.25} L ₇ M _{0.5}	0.75	0.25	7	0.5
N _{0.75} D _{0.25} L ₁₀ M _{0.5}	0.75	0.25	10	0.5
N _{0.75} D _{0.25} L ₅ M _{0.5}	0.75	0.25	5	0.5
N _{0.80} D _{0.20} L ₅ M _{0.5}	0.80	0.20	5	0.0
N _{0.85} D _{0.15} L ₅ M _{0.5}	0.85	0.15	5	0.5
N _{0.90} D _{0.10} L ₅ M _{0.5}	0.90	0.10	5	0.5
N _{0.95} D _{0.05} L ₅ M _{0.5}	0.95	0.05	5	0.5

The solution volume for all syntheses was 100 mL.

Fig. 2a shows the swelling of the nanocomposite hydrogels with different MBAA contents, while other parameters are constant. With 0.1 mmol MBAA, the swelling rate and equilibrium swelling ratio (ESR) of the N_{0.75}D_{0.25}L₅M_{0.1} gel were higher than those with higher MBAA content, except that the N_{0.75}D_{0.25}L₅M_{0.5} gel shows a maximum ESR. This “abnormal” swelling of these gels was repeated several times. In general, the ESR value reflects the crosslink density. The highest ESR of the N_{0.75}D_{0.25}L₅M_{0.5} gel may suggest that the nominal crosslink density in this gel is lower than that in all the remaining gels. Before polymerization, both monomers and MBAA will adsorb on the clay surface. The adsorbed MBAA may reduce the physical adsorption of polymer chains to clay. Meanwhile, it offers additional chemical crosslinking to the network. Thus, there might be a balance between the reduced physical crosslinking and enhanced chemical crosslinking. It is likely that, with 0.5 mmol MBAA, this balance is minimal so that the overall nominal crosslink density is minimal. However, direct evidence is yet to be explored. Interestingly, as seen below, the gels show a maximum strength with 0.5 mmol MBAA.

Fig. 2b shows the swelling behavior of hydrogels with different clay contents. As the clay content in a 100 mL reaction mixture was increased from 2 g to 3, 4, 5, and 7 g, the ESR value decreased from about 32 down to 17. It is interesting that the ESR of the N_{0.75}D_{0.25}L₇M_{0.5} gel was much lower than that of the others, indicating that the crosslink density due to physical adsorption was abruptly increased with 7 g clay in the gel.

Fig. 2c shows the swelling behavior of hydrogels with different NIPAM/DAC molar ratios in 1 mol L⁻¹ monomers, with constant MBAA and clay contents. With the given clay and MBAA contents, or crosslink density, the concentration of ionic monomers plays a critical role in swelling. For example, with 5 g clay and 0.5 mmol MBAA as crosslinkers in a 100 mL reaction mixture, as the DAC concentration was increased from 0.05 mol L⁻¹ to 0.10, 0.15, 0.20, and 0.25 mol L⁻¹ in 1 mol L⁻¹ monomers, the ESR markedly increased from about 2 to 15, 17, 23, and 28 (Fig. 2c). Since the DAC monomers carry permanent positive charges, a higher DAC content rendered higher electrostatic repulsion in the network, and the internal osmotic pressure was enhanced. These features drive a higher water uptake or swelling of the hydrogels.

Mechanical properties of p(NIPAM-co-DAC)/LAPONITE® hydrogels

In the literature, nanocomposite hydrogels usually show very high stretchability and tensile toughness. Less is known about the compressive properties, probably due to the soft nature and lack of load resistance of the physically crosslinked hydrogels. Herein, both compression and tensile tests have been performed to provide comprehensive investigation on the mechanical properties of the p(NIPAM-co-DAC)/clay hydrogels with sparse chemical crosslinking.

Fig. 3 shows representative compressive stress-strain curves, as well as strength and toughness, of hydrogels as functions of MBAA concentration, clay content, and the NIPAM/DAC ratio. As the MBAA content was lower than 1 mmol (in a 100 mL mixture), the fracture strain was higher than 60% and exhibited

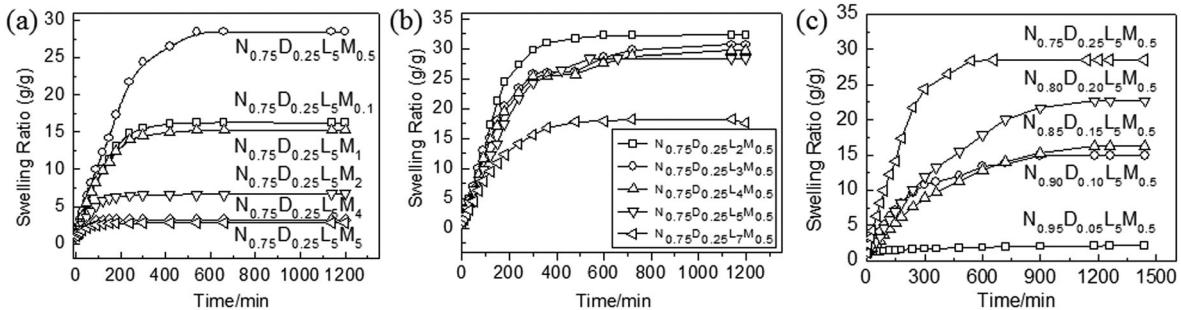


Fig. 2 The swelling of p(NIPAM-co-DAC)/clay hydrogels with different (a) MBA, (b) clay contents, and (c) NIPAM/DAC molar ratio.

a maximum of about 90% with 0.5 mmol MBAA. Correspondingly, the compressive strength of the gels could reach a maximum of about 1.4 MPa (Fig. 3d). Meanwhile, the hydrogel modulus increased monotonically with the MBAA content, indicating an increase in network density with MBAA content. These results suggest that a low MBAA content of 0.05 mmol may be optimal for the compressive properties. For subsequent investigations, the MBAA content of hydrogels was 0.5 mmol in 100 mL reaction mixtures.

In addition to the small amount of chemical crosslinkers, the clay content plays critical roles in the strength and toughness of the hydrogels. Fig. 3b compares the stress-strain curves of hydrogels with clay content from 2, 3, 4, 5, 7, and 10 g in a 100 mL reaction mixture. Most of these nanocomposite hydrogels did not fracture up to a compression strain of 90% or higher, except that the gel with 2 g clay failed at a relatively low strain (82%, Fig. 3b). The compression strength was increased to 6.2 MPa with increasing clay content from 2 g up to 7 g, while it dropped a

bit to 4.5 MPa with 10 g clay (Fig. 3b and e). At a clay content below 4 g, the modulus was decreased with increasing clay content, while it was increased with clay content higher than 4 g.

The molar ratio of NIPAM over DAC showed a remarkable influence on the compressive properties of the gels. Herein, the total monomer concentration was 1 mol L⁻¹, while the molar ratio of NIPAM and DAC was decreased from 0.95:0.05 to 0.85:0.15, and 0.80:0.20. These gels at equilibrium swelling showed fracture strains above 95%, and the fracture strength was decreased with increasing DAC content (Fig. 3c). As demonstrated in Fig. 2c, the ESR for hydrogels was higher with more DAC content, which indicates a higher water content. This explains the decrease in compression strength and modulus with increasing DAC content (Fig. 3f).

The tensile properties of the nanocomposite hydrogels have been systematically investigated. Fig. 4a shows representative tensile stress-strain curves of hydrogels with different clay contents. At low MBAA content, it is interesting that the hydrogels showed

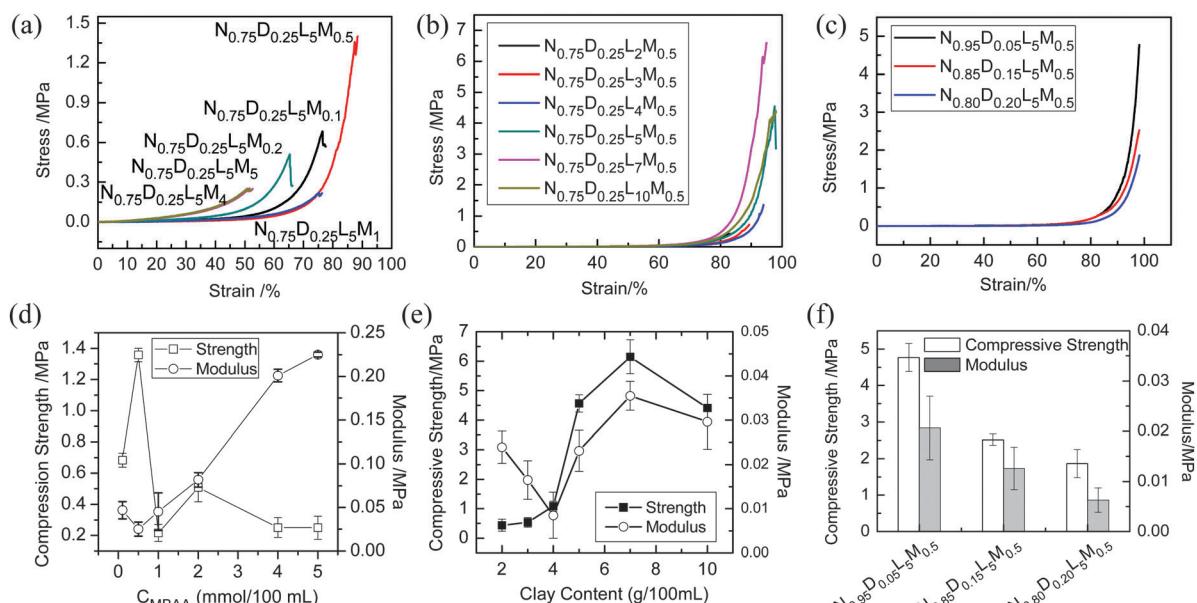


Fig. 3 The compression properties of p(NIPAM-co-DAC)/clay nanocomposite hydrogels. Representative compressive stress-strain curves of hydrogels with different (a) MBAA and (b) LAPONITE® contents, and (c) NIPAM/DAC molar ratio. The effects of (d) MBAA content, (e) LAPONITE® content, and (f) NIPAM/DAC molar ratio on the compressive strength and modulus of the hydrogels.

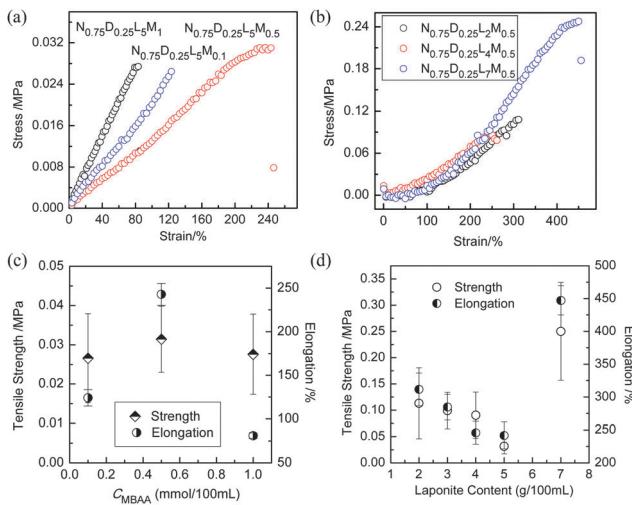


Fig. 4 Representative tensile engineering stress–strain curves of hydrogels with different (a) MBAA and (b) clay contents. The tensile strength and fracture elongation of the nanocomposite hydrogels plotted against (c) MBAA and (d) LAPONITE® contents.

very small difference in tensile strength (in the range of 25–30 kPa, Fig. 4c), whereas the fracture elongation was the maximum (~250%) with 0.5 mmol MBAA. On the other hand, with increasing clay content, the tensile strength was decreased from about 118 kPa to 100, 80, and 40 kPa with 2, 3, 4, and 5 g clay, but abruptly increased to about 250 kPa with 7 g clay (Fig. 4d). Correspondingly, the fracture elongation was decreased from 310% to 280% and 240%, but increased to 450% with 7 g clay.

Multi-responsiveness of the nanocomposite hydrogels

The copolymerization of NIPAM and DAC monomers renders responsiveness to changes in temperature, pH, and ion strength. As a control, the PNIPAM/clay hydrogel showed thermo-responsiveness due to the LCST of PNIPAM chains.²² At temperatures above LCST, the gel became opaque and deswelled due to the increase in hydrophobicity of the chains, while it became translucent when cooled below LCST. The transition temperature (T_{trans}) could be altered by changing the clay content. In this work, T_{trans} was determined by measuring the swelling ratio of hydrogels at different temperatures normalized to that at 20 °C. First of all, in comparison to T_{trans} of about 32 °C³² for the PNIPAM/clay nanocomposite hydrogel, copolymerization of cationic DAC monomers increased the T_{trans} (Fig. 5). For example, T_{trans} of the $N_{0.95}D_{0.05}L_5M_{0.5}$ hydrogel was increased to about 34 °C. As the DAC content was further increased to 10 mol%, 15 mol%, 20 mol%, and 25 mol%, the transition temperature was further increased to about 36, 37, 38, and 41 °C (Fig. 5). The increase in DAC content, or a decrease in NIPAM content, enhanced the hydrophilicity of the hydrogels. As a result, to deswell the gels, a higher temperature is needed for the NIPAM segments to provide adequate hydrophobicity. Other than the DAC content, the effects of MBAA content and clay content on transition temperature were also investigated. Very few changes in the transition temperature were observed with the MBAA and clay contents used in this study (Fig. S2, ESI†).

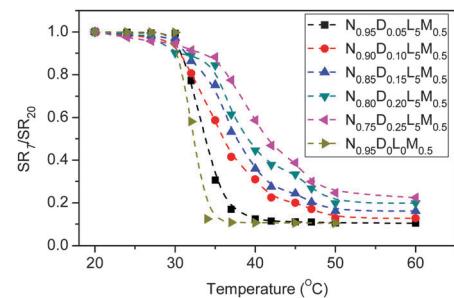


Fig. 5 Swelling ratio (SR_T) of nanocomposite p(NIPAM-co-DAC) hydrogels with increasing temperature normalized against that at 20 °C (SR_{20}).

On the other hand, the presence of DAC units with permanent positive charges renders responsiveness to pH and ion strength of buffer solutions. Experiments were performed by immersing the as-prepared nanocomposite hydrogels into buffer solutions with different pH and ion strength. As the $N_{0.75}D_{0.25}L_5M_{0.5}$ gel, for example, was immersed in Milli-Q water, it started to swell by adsorbing water. After immersing in water for 10 h, the swollen gel was removed and immersed in 0.1 mol L⁻¹ NaCl solution at pH 3. After equilibrium swelling was reached, the gels were separately transferred into 0.1 mol L⁻¹ NaCl solutions with pH 5, 7, 9, and 11. The gels started to shrink slowly. The ESR values of gels at each pH were normalized against that at pH 3 and plotted in Fig. 6. With increasing pH, the gels slightly lose water, probably due to the slight electrostatic shielding by the increasing OH⁻ ions in solution and gel. As the MBAA content was higher, the gels showed less shrinkage at the given pH values. On the other hand, with more DAC content, volume changes due to pH increase were larger (data not provided).

We further demonstrate that these cationic nanocomposite hydrogels are responsive to ion strength changes. Using the $N_{0.75}D_{0.25}L_5M_{0.5}$ gel (1.5 g) as an example, when immersed in Milli-Q water (extremely low ion strength), the initial weight of the as-prepared gel was slightly increased to about 7.6 g in 12 h (Fig. 7). Then, it was transferred into 0.1 mol L⁻¹ NaCl solution, and started to lose water and shrink. Its weight was gradually decreased to about 1.5 g in 16 h. As the gel was removed and immersed in pure water again, it started to re-swell. Such swelling/deswelling cycles were repeated several times, showing excellent reproducibility (Fig. 7). The slight decay in the maximum swelling

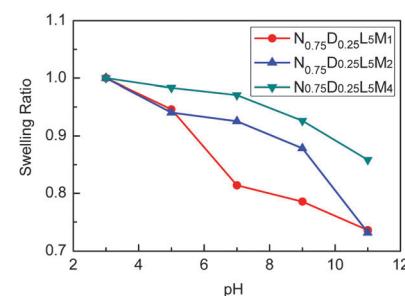


Fig. 6 Normalized swelling ratios of p(NIPAM-co-DAC)/clay hydrogels at different pH values against those at pH 3.

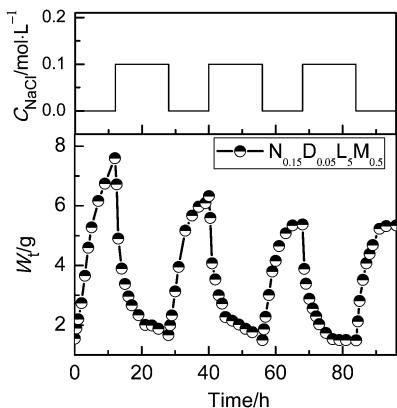


Fig. 7 The oscillatory swelling–shrinking behavior of DN-NC hydrogels upon ion concentration switching between 0 and 0.1 mol L^{-1} .

degree is due to the short swelling time in water. Note that the gel could fully shrink to its original weight and size after various cycles, indicating that no internal rupture or damage occurred during cyclic swelling–deswelling of such strong and tough nanocomposite hydrogels.

As shown in a previous report (PDMAA or PNIPAM), NC gels exhibit swelling behaviors characteristic of a polyelectrolyte gel due to the ionic nature of exfoliated LAPONITE® incorporated in the network, where the degree of swelling changed with salt (*e.g.*, NaCl) concentration in the surrounding aqueous solution.¹⁸ The presence of nanocomposite hydrogels with permanent positive charges exhibits similar changes in swelling with changes in pH and ion strength.

Conclusions

This study demonstrated a successful synthesis of p(NIPAM-*co*-DAC) hydrogels by using cationic monomers in the aqueous solution of LAPONITE® RDS with the presence of a small amount of MBAA as a chemical crosslinker. The obtained nanocomposite hydrogels exhibited high compression and tensile properties due to the synergistic contributions from both physical and chemical crosslinking structures. Surprisingly, such nanocomposite hydrogels showed temperature responsiveness, with the transition temperature varied by changing the NIPAM/DAC ratio. Moreover, the presence of DAC units carrying positive charges rendered outstanding responsiveness to pH and ion strength changes. It is demonstrated that these strong and tough hydrogels could show cyclic swelling/deswelling upon shuttling between solutions with low and high salt concentrations. These multi-responsive nanocomposite hydrogels with excellent strength and toughness may find potential applications in sensors and actuators, controlled drug delivery, and so on.

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